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THE STUDY OF MAGNESIUM/SILVER CHLORIDE
BATTERIES EMPLOYING VARIOUS ELECTRO-
LYTES AND INHIBITORS

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REPORT NO. 702

**THE STUDY OF MAGNESIUM/SILVER CHLORIDE BATTERIES EMPLOYING
VARIOUS ELECTROLYTES AND INHIBITORS**

by

G.D. Nagy and P.J. Powell

Primary Power Sources Section
Electrical Power Sources Division

**PROJECT NO.
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ABSTRACT

Measurements have been made of both temperature and voltage, during and after discharge, on magnesium/silver chloride batteries. These measurements were made on single- and multiple-cell stacks at 45°C. A study of cell behaviour was carried out to determine the possibility of decreasing the corrosion of the magnesium and extending the length of run-out of the present system. An explanation is given for the high corrosion rate of magnesium in 20% LiCl solutions with 0.5% Na₂Cr₂O₇. Possible means of controlling this rate are also presented.

RÉSUMÉ

La température et la tension des piles Mg/AgCl furent mesurées pendant et après leur décharge. Des batteries et des piles simples furent l'objet de l'investigation à une température ambiante de 45°C. Le comportement des piles fut aussi étudié afin de déterminer la possibilité de réduire la corrosion du magnésium et d'améliorer le rendement. La grande vitesse avec laquelle la corrosion du magnésium s'effectuait dans une solution de 20% LiCl et 0.5% Na₂Cr₂O₇ est expliquée et des moyens possibles de la contrôler sont présentés.

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INTRODUCTION

Two of the problems in using magnesium electrodes especially at high temperatures are the high rate of corrosion of magnesium in aqueous solutions and the accumulation of bulky corrosion products. In the AN/URT 503 personal locator beacon battery a 22% LiCl solution (1) is used so that the cell will operate at -40°C . 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$ is added to the electrolyte to decrease the corrosion of magnesium at the upper temperature limit specification, 45°C .

Magnesium batteries and magnesium corrosion have been studied by many investigators but, basic electrochemical and chemical reactions are still in dispute (2-9). Although various electrochemical reactions have been proposed there is no conclusive evidence presented as to the formation of Mg^+ or Mg^{++} or both (4,10-12).

Feitknecht and Held (13) and Newman (14) have studied magnesium corrosion and magnesium complex formation. While they have been able to isolate various hydroxide and hydroxy complexes, very little is known about corrosion products in magnesium/silver chloride batteries. The reason for this lack of information is that in an aqueous medium the corrosion products vary with temperature, time, concentration and electrochemical kinetics of reaction (4,13,14).

Our main interest was in investigating the electrolyte used in the present magnesium/silver chloride system and to see if any improvement in respect to corrosion or run time could be made by changing or adding other compounds to the electrolyte. It was decided that this should be done before proceeding to work involving cell design or improving the magnesium electrode itself, since from a production point of view it appears easier and less costly to change the electrolyte than to give special treatment to the electrode.

EXPERIMENTAL METHODS

The cells used were purchased from the Clevite Burgess Battery Co. and were of the same design they were developing for use with the AN/URT 503 beacon. Each cell consists of two (AZ61A) magnesium sheets (6% Al, 1% Zn and 0.2% Mn) 0.033 in. by 2-5/8 in. by 3 in. and one AgCl sheet 0.055 in. by

2-5/8 in. by 3 in. The AgCl plate was sandwiched between the two magnesium plates. Separation of 1/16 in. was maintained by two plastic bars 1/16 in. by 3/32 in. by 2 in. on each side of the AgCl plate. The individual cell stacks were completely sealed with Mylar, an adhesive insulating tape, except for two 1/16 in. diameter by 1 in. long ports at the top and bottom of the cells intended to allow electrolyte to enter the cells when activated.

The cells were discharged in individual lucite cases, 3-1/2 in. by 4-1/4 in. by $n(7/16)$ in., where n is the number of cells in the battery stack.

The electrolytes were made from reagent grade chemicals and distilled water. All percentages quoted are on a weight basis.

Cells were run at $45^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ and the voltages and the temperatures within the cell recorded. The temperatures were monitored by a YSI resistance thermometer coupled to a Vibron electrometer and an Esterline-Angus recorder.

Before an initial discharge began, the cells, electrolyte and container were preheated to 45°C . Then the cells were placed into their plastic containers and activated under load by adding 40 mls of electrolyte per cell. The cells were discharged at 140 mA for a period of 4 h/day, then left on open circuit for the remaining 20 h/day. The end-voltage was chosen to be 1.1 volt per cell.

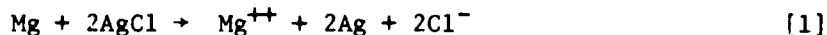
Theoretically these magnesium/silver chloride cells should run for 46.3 hours or 11.4 days on intermittent load. This calculation is based on the amount of AgCl present. If magnesium corrosion and inter-cell shorting were eliminated, the magnesium theoretically would last for 200 hours or 50.0 days on the intermittent load. This calculation assumes that all of the magnesium is oxidized to the divalent form.

RESULTS AND DISCUSSION

Lithium Chloride Electrolytes with No Inhibitors

Figure 1 shows the temperature recorded in a single cell (solid curves) and a two-cell pack (dashed curve) on intermittent load at 45°C in which the electrolyte was 20% LiCl, i.e. no inhibitor. The curves for each 24-hour period are superimposed. For the single cell, the temperature on the first day reached 52.2°C at the end of discharge and decreased during the open circuit period. Similar, but smaller temperature increases were noted during successive discharges. After 2 hours of discharge on the 4th day the cell reached 1.1 volt, for a total of 14 hours discharge.

Dissection of the cell after run-out showed that about 10% of the magnesium remained intact as metal. Seven per cent had been used for the electrochemical reaction,



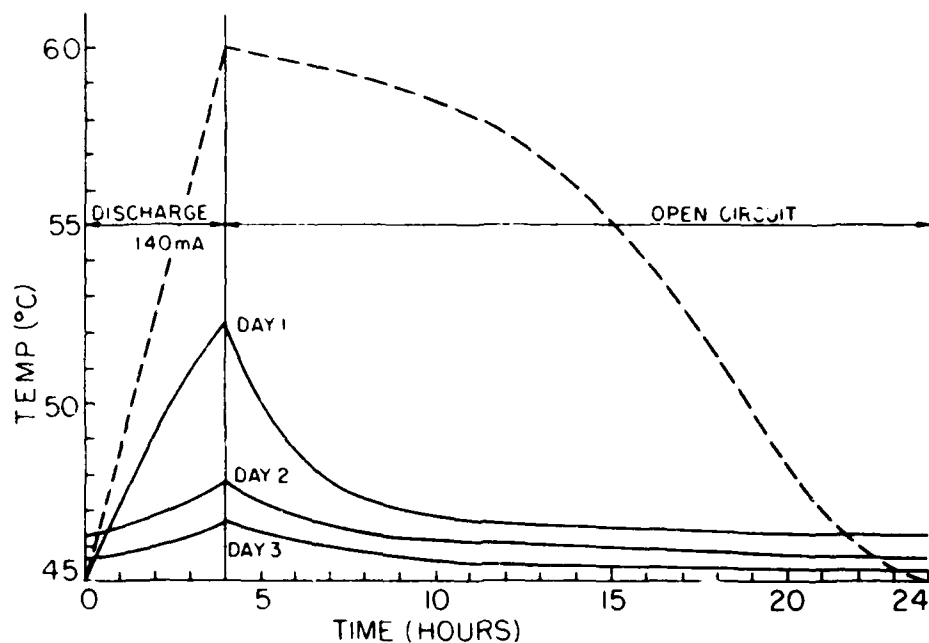


Figure 1: Temperature-Time curve for a one cell pack (solid curves) and a two cell pack (dashed curve) containing 40 mls of electrolyte (20% LiCl, no inhibitor) per cell.

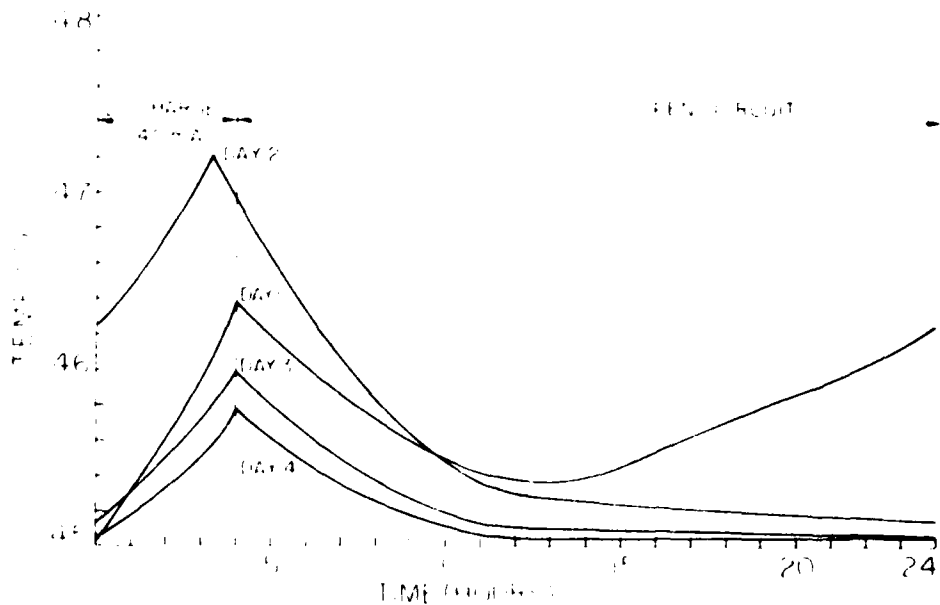


Figure 2: Temperature-Time curve for a one cell pack containing 40 mls of electrolyte (20% LiCl plus 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$ as an inhibitor).

and the remaining 83% was consumed by the corrosion reaction,



The standard heats of reaction at 25°C for reactions [1] and [2] are -129.74 and -110.41 Kcal/mole respectively (15). The theoretical open-circuit voltage of the cell is 2.63V and the average run-out voltage was 1.50 volts. Therefore, at most, 56 Kcal/mole

$$\left(\text{that is, } \frac{129.74 (2.63 - 1.5)}{2.63} \right)$$

of the heat liberated would be due to reaction [1] within the cell at 25°C. The majority, greater than 96%

$$\left(\text{that is, } \frac{0.83 \times 110.41 \times 100}{0.83 \times 110.41 + 0.07 \times 56} \right)$$

of the heat generated in the cell was due to the corrosion reaction [2]. Less than 4% was due to reaction [1].

The lower temperatures, at the same point in successive discharges, indicate that the rate of corrosion decreases with time. The increase in temperature during the discharge part of the daily cycle can be explained on the basis of the "negative difference effect" discussed by Robinson and King (6). Fresh electrode without any passivating layer is being exposed to the electrolyte.

The dashed curve of Figure 1 shows the temperature increase during operation of a two-cell pack in 20% LiCl solution. When put on load at the start of the second discharge the cell voltage fell below the cut-off voltage. The volume, number of cells, amount of electrolyte, heat capacity and amount of heat liberated will be twice as great for a two-cell pack as for a one-cell pack. However, because of the dimensions of the plastic container, the area through which the heat flows to the environment increases by a factor of only 1.19 (36.5 square inches for a one-cell pack and 43.3 square inches for the two-cell pack). This difference in the heat flow parameters and intercell shorting can account for the higher temperature of the two-cell pack compared to the single cell. The higher temperature within the cell will have the detrimental effect that the rate of corrosion magnesium will be greater.

Lithium Chloride Electrolytes with Sodium Dichromate Inhibitor

Figures 2 to 4 show the temperature changes during discharge of one-, two- and three-cell packs, in which the electrolyte was 20% LiCl plus 0.5% Na₂Cr₂O₇ in all cases. The discharge times were 18.0, 17.75 and 17.5 hours respectively. As indicated by the smaller temperature increases, compared to Figure 1, and the longer run-outs, the rate of corrosion was lowered.

It can be seen that on the 1st day at 12 to 16 hours the rate of corrosion began to increase. At the same time it was noted that the colour of the solution was that characteristic of a chromate and not a dichromate, and that the pH had risen from 3.5 to 7.2. At a pH of 7.2, the chromate should be the predominant species (4). These changes are very likely due to the reaction [2] which would increase the pH and affect the equilibrium reaction.

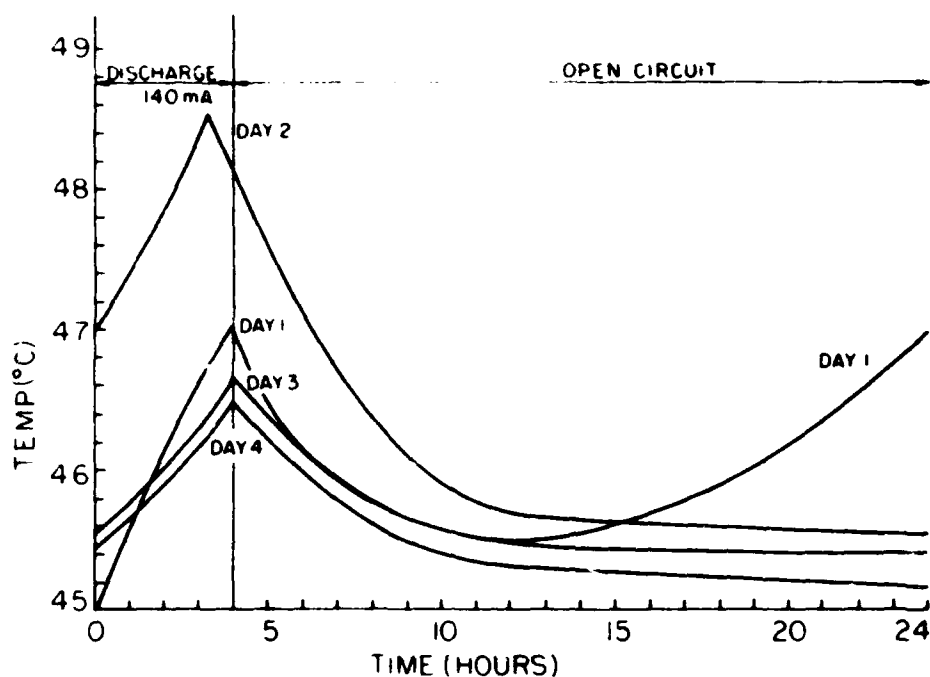


Figure 3: Temperature-Time curve for a two cell pack containing 80 mls of electrolyte (20% LiCl plus 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$).

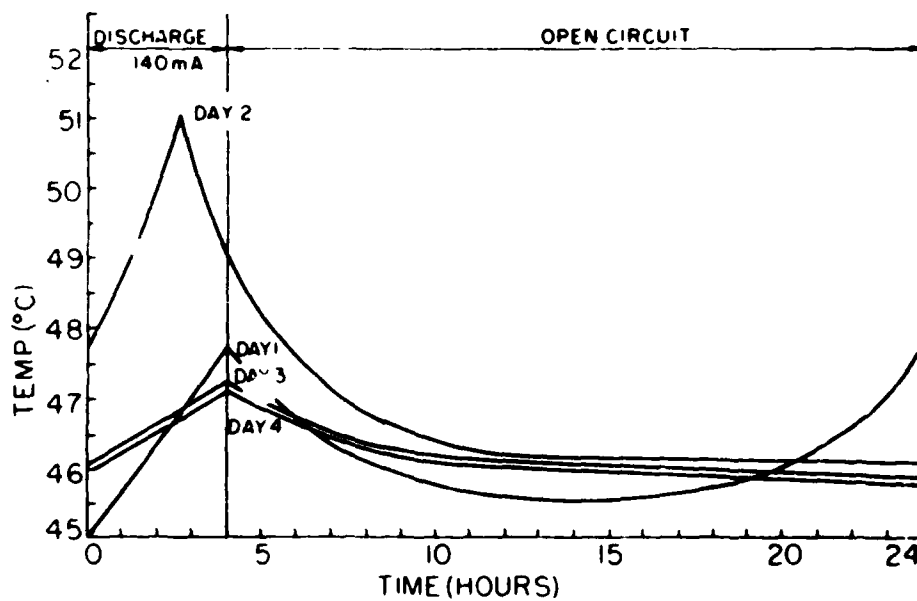
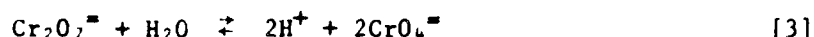


Figure 4: Temperature-Time curve for a three cell pack containing 120 mls of electrolyte (20% LiCl plus 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$).



It was first considered that the rise in temperature on open circuit at about 12 to 16 hours was due to the fact that the chromate may be a poorer inhibitor than the dichromate. However, this is not the case, as Figures 2 and 5 show that for a one-cell pack $\text{Cr}_2\text{O}_7^{=}$ and $\text{CrO}_4^{=}$ work equally well as inhibitors. Both runs show almost identical changes in temperature, including an increase in the corrosion rate at about 13 hours after activation. Because of reaction [2], the pH at the magnesium electrode/electrolyte interface may be sufficiently high that the dichromate in the vicinity of the magnesium electrode is partially or totally converted to the chromate. The specific species doing the inhibiting may be the chromate or a combination of dichromate and chromate.

Temperature Anomalies in Lithium Chloride Electrolytes

Figure 6 shows that the temperature rise experienced by cell-packs in the 13-to 28-hour time period after activation is not due to the physical state of the magnesium electrode. Thus, in this experiment, a one-cell pack was activated under load, discharged for four hours and allowed to stand on open circuit for 20 hours. It was then taken apart and the magnesium and silver chloride plates washed lightly, rebuilt into a new cell and run-out using fresh electrolyte. As can be seen the electrode behaved identically in the two portions of fresh electrolyte during the first twenty-four hours. On subsequent days the rebuilt cell behaved as if it were a new cell even showing a peak at about 28 hours. This indicates that changes in the electrolyte cause the rise in temperature at about 13 hours after activation.

Figure 7 shows the temperature of a single cell which was filled with electrolyte (20% LiCl plus 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$) and left on open circuit for 30 hours. As in the case of a cell which experienced 4-hour intermittent discharges, two temperature-peaks were observed, and in the vicinity of the second peak the colour of the solution was green, characteristic of a chromate salt. The main difference between cells under discharge and the cell which stood on open circuit (Figures 2 and 7) was that the first temperature-peak was much higher. This curve bears a resemblance to the curve shown in Figure 8 obtained by Casey and Bergeron (16) for the rate of corrosion of magnesium in MgCl_2 solutions as a function of MgCl_2 concentration. Figure 8 was obtained at 25°C and at an initial pH of 2.0. These investigators found that below 1 molal the rate of corrosion was dependent upon the MgCl_2 concentration and also upon the pH of the solution. At concentrations greater than 1 molal the rate of corrosion was dependent upon the MgCl_2 concentration but independent of the pH. The initial corrosion rates of magnesium in MgCl_2 solutions differ from those in aqueous KCl and KNO_3 solutions, and indeed the same is true for many metals in aqueous salt solutions (10-12,17,18). The rates of corrosion in the latter cases show only one maximum in the rate-versus-molality curve, usually at concentrations below 1 molal. The rate of corrosion also decreases as the pH increases.

In the system we are using the rate of corrosion will be initially controlled by the concentration of LiCl and $\text{Na}_2\text{Cr}_2\text{O}_7$ in the solution.

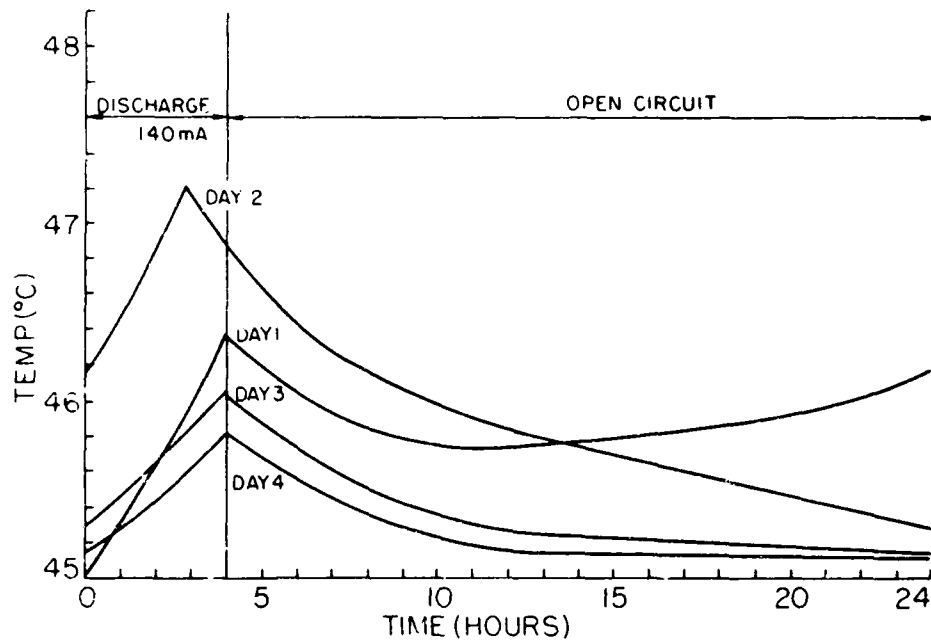


Figure 5: Temperature-Time curve for a one cell pack containing 40 mls of electrolyte (20% LiCl plus 0.5% Na_2CrO_4).

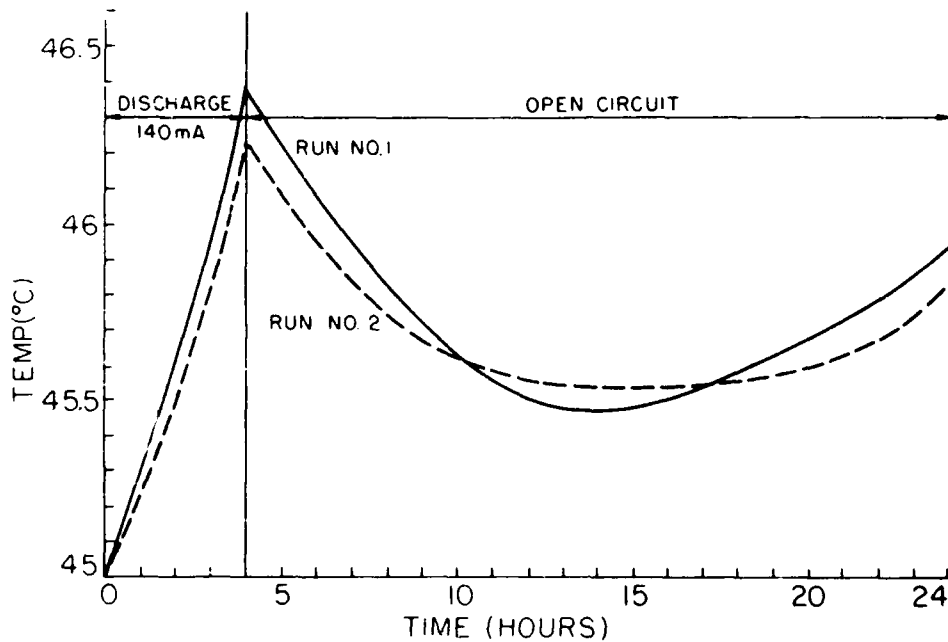


Figure 6: Temperature-Time curve for a one cell pack containing 40 mls of electrolyte (20% LiCl plus 0.5% Na_2CrO_4). Run 1, Fresh cell. Run 2, same cell after 29 hours, but rinsed with distilled water and rerun in fresh electrolyte.

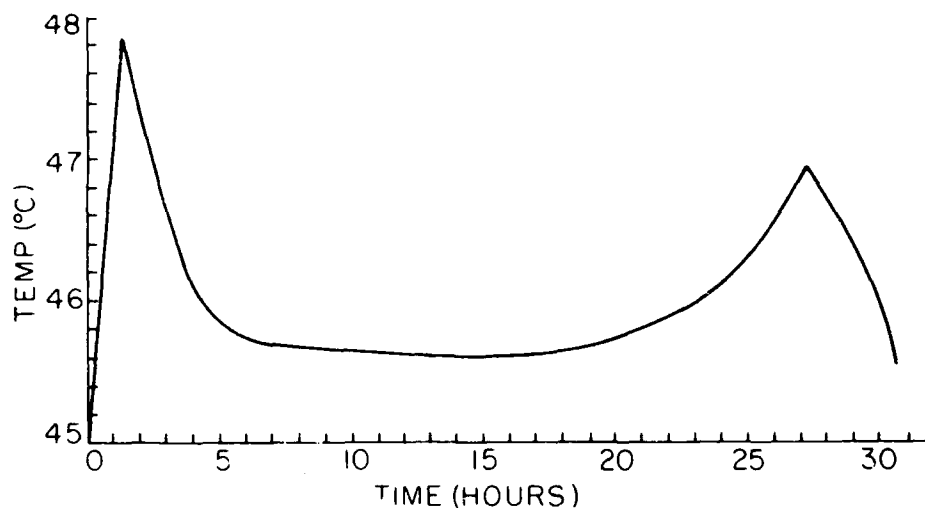


Figure 7: Temperature-Time curve for a one cell pack containing 40 mls of electrolyte (20% LiCl plus 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$). This cell was activated on open circuit and left on open circuit for 30 hours.

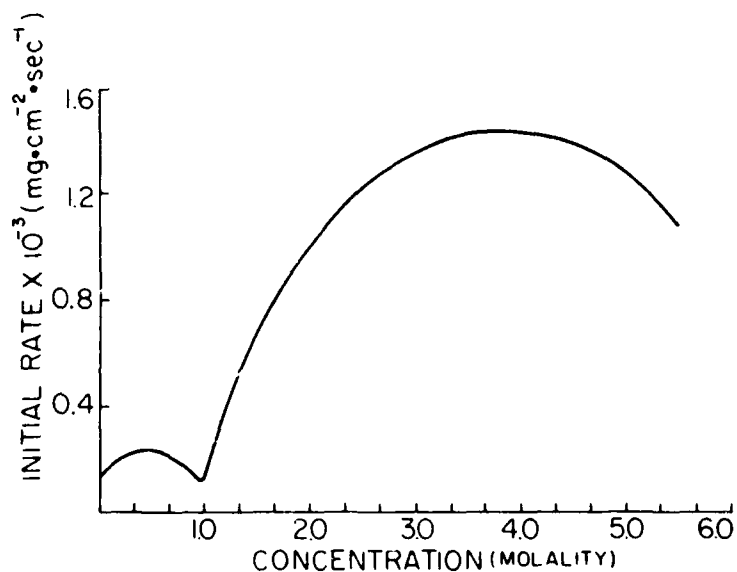


Figure 8: Initial Rate of Dissolution of flat, horizontal corroding faces of magnesium as a function of concentration of MgCl_2 , pH 2.0, 25°C. (see ref 16).

Because of the position of lithium in the periodic table relative to potassium and sodium we would expect the initial rates of corrosion of magnesium in the chlorides of these three salts to be similar. However, as corrosion of magnesium proceeds and as magnesium builds up in the electrolyte one might expect to find the same phenomena as observed in solutions originally containing magnesium ions. Therefore, the possibility of two humps occurring in the temperature-versus-time curves exists. Changes in pH, the presence of LiCl and the presence of solid corrosion product may account for the fact that in Figure 7 the temperature of the second peak and hence the corrosion rate is lower than that of the first.

To determine that the temperatures of the cells on open circuit above 45°C (i.e. above the ambient temperature of the oven), were due to corrosion and not thermal lag, the following experiment was carried out. A cell which had been given three discharges and then left on open circuit for 20 hours at 45°C was heated to 47.0°C then allowed to cool to 45°C in the oven. Then it was cooled to 43°C and allowed to warm up to 45°C in the oven. In both cases the temperature was within 0.1°C of the ambient within thirty minutes. Comparing these values to Figure 2 it can be seen that after the discharge period there must be some source of heat, namely the corrosion of magnesium, keeping the cell from cooling directly to the ambient temperature.

The cell, whose run-out is shown in Figure 2, was dissected after the voltage reached 1.1 volt. It was determined that 82% of the magnesium had corroded and 8% was used for the electrochemical discharge reaction. An estimation of the amount of corrosion at any time can be made if one treats the temperature-time curves as thermograms, integrates under the curve, applies the law of conservation of energy and makes the following assumptions:

- 1) When the cell is at the ambient temperature, there is no internal source of heat and hence, the corrosion of magnesium is negligible.
- 2) Temperatures above the ambient are due to corrosion of the magnesium and the rate of corrosion is proportional to the difference in the temperature between the cell and ambient, at least to a first approximation.
- 3) During discharge the heat liberated within the cell due to the electrochemical reaction [1] is one-half that of the corrosion reaction [2] (See calculations of heats of reaction on page 4).

Therefore, graphical integration of Figure 2, in which 86% of the magnesium (that is, 0.990 equivalents) which gives rise to heating at the rate of 110 Kcal/mole, yields an area of 45.2°C-h. The proportionality factor relating amount of corrosion to the area under the curves is therefore 0.022 eq/(°C-h).

Forty ml. 11litres of electrolyte was used for each cell. On this basis, the corresponding proportionality factor relating the change in the average concentration of $MgCl_2$ to the area under the curve is 0.31 molal/°C-h. Table 1 lists the average concentrations for various times during the run-out. The agreement between the average concentrations at the temperature peaks at 4 and 28 hours and that of the maximum corrosion rates in Figure 8 is satisfactory considering that the pH of the solution is not constant and that the concentrations near the electrode will be different than the average concentration. However since the diffusion rates of magnesium ions for the

TABLE I

Average Concentration of Mg^{++} in Solution at Various Times During Run
(See Figure 2)

	<u>Total Time</u> <u>after activation</u>	<u>Total Average Concentration</u> <u>(molal)</u>
End of 1st discharge	4 hours	0.81
During OC after 1st discharge	13 hours	2.85
Start of 2nd discharge	24 hours	5.40
End of 2nd discharge*	28 hours	7.65
Start of 3rd discharge	48 hours	10.54
End of 3rd discharge	52 hours	11.19
Start of 4th discharge	72 hours	12.56
End of 4th discharge	76 hours	13.01
Start of 5th discharge	96 hours	13.92

* The peaks in the temperature-time curves for day 2 of Figures 2 to 5 all occur before the end of the discharge. This indicates that the maximum corrosion rate in these cases are attained during the second discharge.

two cases should be similar, the concentration near the electrode and the samples used in Figure 8 should be comparable. The rate of corrosion of the magnesium is therefore very dependent upon the magnesium ion concentration.

For the first discharge of Figure 2, 0.021 equivalent of magnesium was used in the electrochemical reaction. Based on the area under the curve and the figure of 0.022 eq/°C-h), one calculates that 0.057 equivalent of magnesium was "corroded". Because the heat produced per equivalent for the magnesium oxidized electrochemically is one-half that of the corroded magnesium (assumption 3) above), in reality 0.047 equivalent was corroded. Similarly, for day 4 one can calculate that 0.021 equivalent of magnesium was consumed for each of the reactions. Thus it can be seen that the majority of the heat generated during discharge is from the corrosion reaction (82% for day 1 and 66% for day 4).

Magnesium Chloride Electrolytes, with and without Inhibitor

Figures 9 and 10 show the effect of 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$ on the temperature rise of one-cell packs in 20% MgCl_2 . Because of the similarity of the temperature-time curves for days 2 to 8, only curves for days 2, 5 and 8 are shown in Figure 10. The temperature during discharge gradually decreased with each succeeding day. Twenty percent MgCl_2 was chosen so that during the first discharge the average concentration of magnesium in the solution, and therefore in the vicinity of the electrolyte, would be 4 molal, i.e. at the concentration for the maximum rate of corrosion in Figure 8. Twenty percent MgCl_2 solution is not a suitable electrolyte for the AN/URT 503 personal locator beacon because it freezes at -33°C . It was used here for comparison with LiCl and to determine the effect of high initial MgCl_2 concentration on the rate of corrosion of magnesium.

From Figure 9 one would infer the corrosion rate to be very high, and in fact, only one day's run could be obtained. Five major differences were noted in the temperature-time curves for cells with 20% MgCl_2 plus inhibitor (Figure 10) when compared to cells with LiCl plus inhibitor. First, no temperature peak at 16-28 hours was observed. Secondly, the maximum temperature was observed after only one hour, at a time when the magnesium ion concentration in the solution, especially in the vicinity of the electrode, would be expected to be greater than 4 molal. Thirdly, the falloff in temperature after a discharge was more rapid. Fourthly, there was less corrosion product which was darker and more gelatinous. The different type and amount of corrosion product may allow the inhibitor better access to the magnesium and account for the more rapid decrease in temperature during open circuit immediately after the discharges. Finally, the cell ran for 35 hours at which time the AgCl was used up while about one-half of the magnesium was still present. Water had to be added after 28 hours of discharge (i.e. the 7th day) because the solution had fallen below the temperature probe. It is realized that the addition of water is undesirable, but the run was continued to see if the AgCl was the limiting electrode.

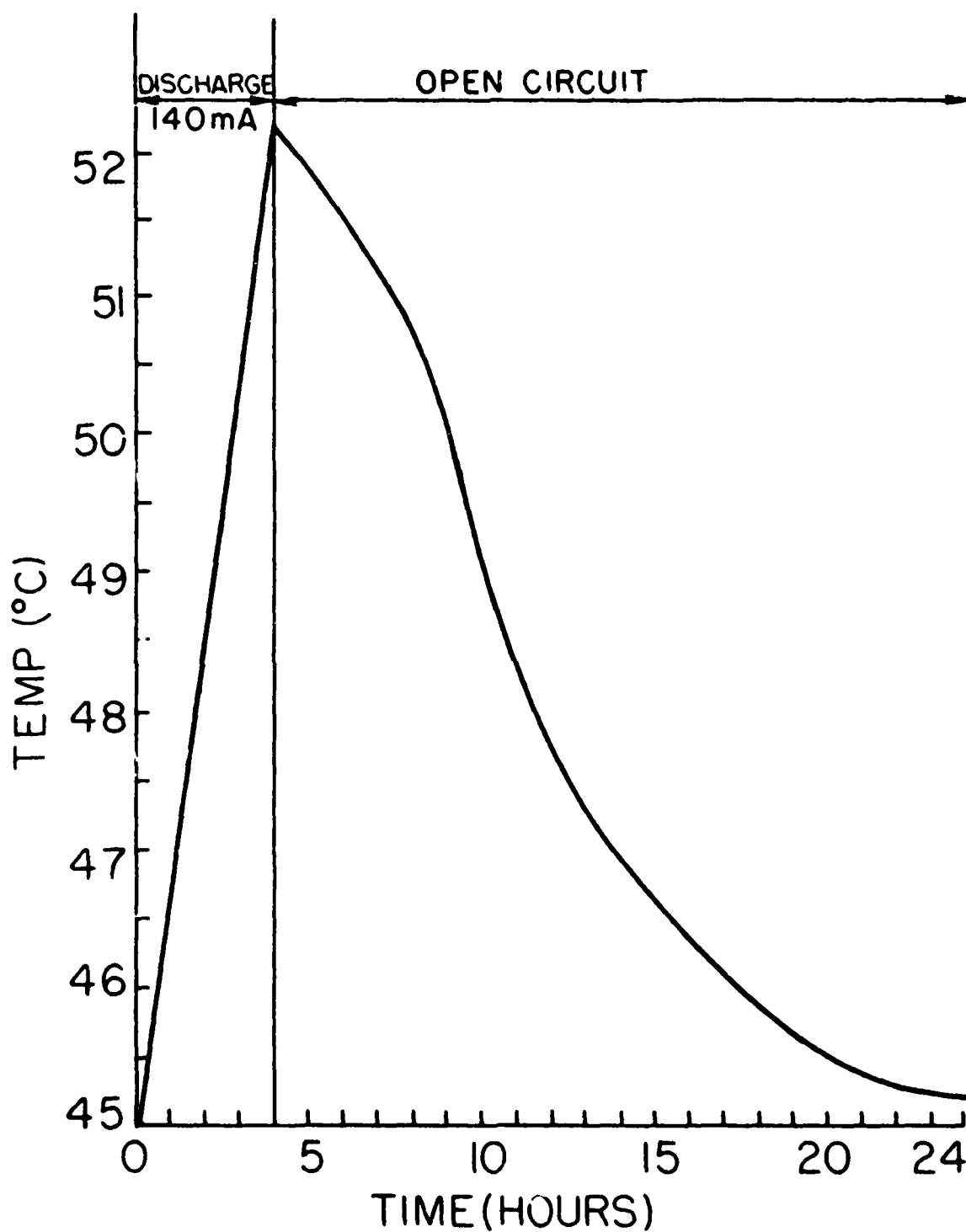


Figure 9: Temperature-Time curves for a one cell pack containing 40 mls of electrolyte (22% MgCl_2).

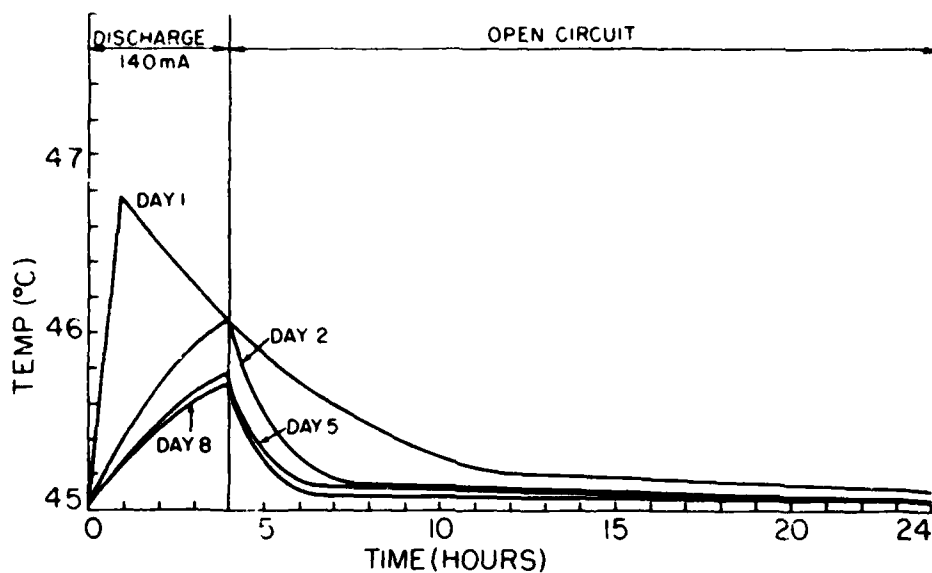


Figure 10: Temperature-Time curves for a one cell pack containing 40 mls of electrolyte (20% MgCl_2 plus 0.5% $\text{Na}_2\text{Cr}_2\text{O}_7$).

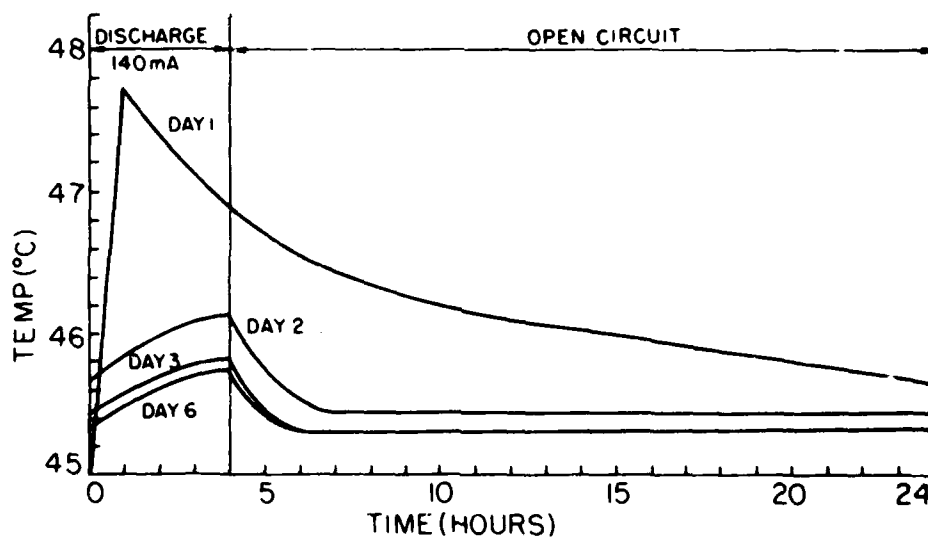


Figure 11: Temperature-Time curves for a one cell pack containing 40 mls of electrolyte (10% MgCl_2 , 20% LiCl plus 0.25% $\text{Na}_2\text{Cr}_2\text{O}_7$).

Mixed Electrolytes

It was indicated earlier that the presence of high concentrations of MgCl_2 in the LiCl electrolyte can decrease the rate of corrosion of magnesium. Therefore mixed electrolytes containing the two salts should be beneficial. Figure 11 shows the temperature-time curves for run-outs of a single cell in 10% MgCl_2 , 20% LiCl plus 0.25% $\text{Na}_2\text{Cr}_2\text{O}_7$ at 45°C . Only one curve for days 3 to 6 is shown as they were virtually identical. This cell ran for approximately 26 hours on intermittent load when it failed due to lack of electrolyte. There was considerably less corrosion of the magnesium when compared to LiCl electrolytes with twice as much dichromate inhibitor.

Work on mixed electrolyte systems has been continued at 45°C and -40°C . A compromise had to be worked out to obtain a good electrolyte at 45°C but one which will not freeze at -55°C during storage or at -40°C during discharge. Since MgCl_2 is formed during discharge and the electrolyte is near the eutectic composition, the freezing point of the electrolyte will increase during discharge.

Buffered Electrolytes

One change that occurs at 45°C is the increase in pH and formation of a basic precipitate that fills the cell. It was reasoned that organic buffers might keep the pH lower and extend the run out. Tartaric and citric acid were considered to be possible buffers. However, when these acids were added to a mixed electrolyte containing LiCl , MgCl_2 and $\text{Na}_2\text{Cr}_2\text{O}_7$, a precipitate formed in a few hours. Although the precipitates were not analyzed, they could have a detrimental effect on the shelf life of the electrolyte, and on the activation of the battery, so this approach was abandoned.

CONCLUSIONS

- (1) An inhibitor is necessary in magnesium batteries in lithium chloride electrolytes at 45°C . Chromates and dichromates are equally effective.
- (2) The temperature-increases in the cell are primarily due to corrosion of the magnesium.
- (3) The peak in the temperature at 20-28 hours in LiCl solutions is related to the concentration of magnesium ions in the electrolyte, and the corrosion rate of magnesium reaches a maximum at this time.

- (4) By adding magnesium ions to the electrolyte the amount of corrosion of magnesium can be lowered.

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